

CERTIFICATE

I, Toshio NISHIZAWA, a citizen of JAPAN, residing at, 4-3-14, KUDAN-KITA,
CHIYODA-KU, TOKYO, JAPAN hereby certify that I am conversant with the
English and Japanese language, and I further certify that to the best of my
knowledge and belief the foregoing is a true and correct English translation of the
Japanese Patent Application No. JP 2004-25121, attached hereto.

Signed this 8th day of December, 2008


Toshio NISHIZAWA

[Title of the document] Scope of claims

【claim 1】 A methanol-reforming catalyst, characterized by containing an intermetallic compound Ni₃Al.

【claim 2】 The methanol-reforming catalyst according to Claim 1, characterized by containing the intermetallic compound Ni₃Al and coexistent components, wherein the contents of Ni and Al are respectively 77 to 95% and 5 to 23% with respect to the total element composition (wt %) including the coexistent components.

【claim 3】 The methanol-reforming catalyst according to Claim 1 or 2, characterized by being a powder or granule prepared by machining and mechanically polishing a melt-prepared ingot or in an atomization process.

【claim 4】 The methanol-reforming catalyst according to any one of Claims 1 to 3, characterized by being alkali or acid treated.

【claim 5】 A methanol-reforming method by using the catalyst according to any one of Claims 1 to 4, characterized in that hydrogen is produced by bringing methanol or a liquid mixture of methanol and water into contact with the catalyst.

【claim 6】 The methanol-reforming method according to Claim 5, wherein the methanol or the liquid mixture of methanol and water is brought into contact with the catalyst that is previously subjected to a hydrogen reduction treatment.

【Title of the document】 Specification

**【Title of the invention】 INTERMETALLIC COMPOUND Ni₃Al CATALYST
FOR REFORMING METHANOL AND METHANOL REFORMING METHOD
USING SAME**

【Field of the invention】

The present invention relates to a methanol-reforming catalyst useful in producing hydrogen and a methanol-reforming method using the same.

【Background Art】

Recently, hydrogen, which generates only water in combustion, is attracting attention as a clean energy medium from the viewpoint of preservation of the global environment and more recently as a fuel for fuel cell. Various methods of producing hydrogen as a fuel are known, and one of them is a method of producing hydrogen in a methanol-reforming reaction. Although methanol may be used as it is as a biomass fuel or the like, methanol as a source of hydrogen by reforming is attracting attention from the viewpoint of energy efficiency.

The reaction of producing hydrogen by reforming methanol is endothermic, and, for example in a methanol-reforming gas engine of fuel cell-powered vehicles, exhaust heat is used for raising the temperature of the methanol-reforming reaction for improvement in energy utilization efficiency, and the overall efficiency in such a case is said to be improved by 31-48%, compared to the case where methanol is directly combusted.

However, when the exhaust gas is used actually for the methanol-reforming reaction, a low-cost longer-lifetime catalyst superior in heat resistance, activity, and abrasion resistance is needed, because the temperature of the exhaust gas fluctuates in the range of 200 °C to 700°C. Base metal elements

such as copper, chromium and zinc or the oxide thereof have been generally used as the methanol-reforming catalysts, but although active at low temperature in the reforming reaction for producing water vapor from methanol, these conventional catalysts have a problem of low heat resistance. Alternatively, catalysts of a noble metal element (e.g. platinum) or the oxide thereof supported on a carrier such as alumina are also known, but these catalysts have a problem of high cost.

Under the circumstance surrounding the conventional technology described above, the present inventors paid attention to an intermetallic compound Ni₃Al superior in high-temperature properties and abrasion resistance the yield strength of which has a positive dependence on temperature (called reverse temperature dependence of strength) as a methanol-reforming catalyst. The intermetallic compound Ni₃Al has been proposed as a molded catalyst (patent document 1), but the potential thereof as a methanol-reforming catalyst at high temperature is not studied and there was no report on such applications.

[Patent document 1] Japanese Patent Application Laid-Open No. 55-88856

[Disclosure of invention]

[Problems to be solved by the invention]

An object of the present invention, which was made under the circumstances above, is to provide a new low-cost methanol-reforming catalyst for producing a hydrogen-containing gas from a raw material, methanol or a liquid mixture of methanol and water, which is superior in heat resistance and abrasion resistance and has a high activity and high selectivity even at high temperature, and a new methanol-reforming method using the same.

[Means for solving the problems]

In order to achieve the above-described object, a first aspect of the present

invention provides a methanol-reforming catalyst characterized by containing an intermetallic compound Ni₃Al.

In a second aspect, the present invention provides a methanol-reforming catalyst, characterized by containing the intermetallic compound Ni₃Al and coexistent components, wherein the contents of Ni and Al are respectively 77 to 95% and 5 to 23% with respect to the total element composition (wt %) including the coexistent components. In a third aspect, the present invention provides a methanol-reforming catalyst, characterized by being a powder or a granule prepared by machining and mechanically polishing a melt-prepared ingot or in an atomization process. In a fourth aspect, the present invention provides the methanol-reforming catalyst in any one of the aspects above, characterized by being alkali or acid treated. In a fifth aspect, the present invention provides a methanol-reforming method by using the catalyst in any one of the aspects above, characterized in that hydrogen is produced by bringing methanol or a liquid mixture of methanol and water into contact with the catalyst.

In a sixth aspect, the present invention provides a methanol-reforming method, characterized in that methanol or a liquid mixture of methanol and water is brought into contact with a catalyst that is previously subjected to a hydrogen reduction treatment.

[Effect of the invention]

As described above, the first invention in this application provides a methanol-reforming catalyst containing an intermetallic compound Ni₃Al that is superior in activity and selectivity even at a temperature of 350°C or more in the reaction producing a hydrogen-containing gas from methanol or a mixed liquid of methanol and water as the raw material.

In the second invention, the catalyst may contain other coexistent components in amounts in particular ranges in addition to the intermetallic compound Ni₃Al, which allows production and preparation of the catalyst easier and at low cost.

In the third invention, it is possible to produce a powdery or granular catalyst that is more easily applicable to the methanol-reforming reaction by employing more convenient means.

In addition, the fourth invention allows improvement in the surface activity of the active ingredient intermetallic compound and modification of the surface shape and composition thereof, consequently leading to improvement in catalytic activity even at a lower temperature.

Further, the fifth and sixth inventions of this application allow efficient hydrogen production because of the highly reactive methanol-reforming reaction when the catalyst is used actually at a high temperature of 350°C or more.

[Mode of practice of invention]

Embodiments of the present invention that is characterized as described above will be described hereinafter.

In the catalyst according to the present invention containing the intermetallic compound Ni₃Al as active component, the compositional ranges of Ni and Al in independent phases are respectively 85 to 88 wt % and 12 to 15 wt %. The catalyst containing the Ni₃Al intermetallic compound may contain additionally other components: for example, NiAl, Ni₅Al₃, Ni, and the like. Allowed presence of these components makes preparation and adjustment of the catalyst easier and is also favorable for adjustment of the composition and the shape of catalyst and for activation treatment. When these other components are present, the overall

compositional ranges of Ni and Al are preferably 77 to 95 wt % and 15 to 23 wt %, respectively.

Also in the present invention, the intermetallic compound Ni₃Al may be treated with an alkali or acid, for removal of the oxide on the surface of the intermetallic compound Ni₃Al or the like, control of the surface shape and the composition and enhancement of catalytic activity by dissolving Al and Ni. The alkali treatment is generally performed by using an aqueous solution or an organic solvent solution of an inorganic or organic base and at a temperature in the range of room temperature to approximately 100°C. Alternatively, an aqueous solution or an organic solvent solution of an inorganic or organic acid can be used for the acid treatment. The processing temperature is generally considered to be room temperature to approximately 50°C.

In the alkali treatment, only Al is dissolved and Ni remains almost undissolved. For example when an aqueous NaOH solution is used, the concentration of NaOH is preferably 10% or more, more preferably 20 to 30%; the processing temperature, 60-100°C; and the processing period, 1 hour or more. In the acid treatment, both Al and Ni are dissolved, and care should be given to the treatment, because processing at a higher concentration for an extended period often results in increase in loss of the intermetallic compound Ni₃Al. For example, when a HCl solution is used, the concentration is preferably 20% or less; the processing temperature, around 20°C; and the processing period, 1 hour or less. When a HNO₃ solution is used, the concentration is preferably 5% or less; the processing temperature, around 20°C; and the processing period, 1 hour or less.

The methanol-reforming catalyst according to the present invention can be produced or prepared by various methods. For example, a powder or granule

thereof can be produced, for example, by forming the raw metal elements into the shape of ingot and machining the raw ingot and additionally mechanically polishing the powder or granule thus obtained, or in the atomization process from the molten metal. The powder or granule thereof may of course be molded into a desirable shape. The catalyst may also contain ceramics, other metals, and the complexes thereof additionally. Any one of other methanol-reforming catalysts including known catalysts may be used in combination, as long as it does not inhibit the activity of Ni₃Al.

When the catalyst according to the present invention described above is used in the shape of powder or granule, the average diameter of the catalyst is, for example, in the range of approximately 150 µm or less and more preferably 32 µm or less. The specific surface areas thereof are, for example, in the range of 2.5 m²/g or less before the alkali or acid treatment and in the range of 2.5 to 6 m²/g after treatment.

Methanol or a liquid mixture of methanol and water may be used in producing hydrogen in the methanol-reforming reaction by using the catalyst according to the present invention. When methanol and water are used, the ratio of methanol to the catalyst (methanol:water) is generally, for example, approximately 1:0.1 to 5 as a molar ratio at a space velocity (LHSV) in the range of 15 to 35 h⁻¹. The reforming reaction may be carried out by a fixed-bed or fluidized bed method.

The reaction temperature is more preferably in the range of 240°C to 400°C.

Hereinafter, the embodiments of the present invention will be described in more detail with reference to the following Examples, but it should be understood

that the present invention is not restricted by the following Examples.

[Example]

<Example 1>

The following two kinds of Ni₃Al powder samples were prepared:

(a) A Ni₃Al powder sample having a composition of 86.91 wt % Ni and 13.09 wt % Al was prepared in a rotating disk atomization process. The specific surface area of the powder having a particle diameter of 32 µm or less as determined by the BET method was 1.3 m²/g; the specific surface area of the powder having a particle diameter of 32 to 75 µm was 0.4 m³/g; and the specific surface area of the powder having a particle diameter of 75 to 150 µm was 0.1 m²/g.

(b) A Ni₃Al alloy ingot having a composition of 87.32 wt % Ni and 12.67 wt % Al was prepared in a melting furnace. Chips were produced from the ingot by machine work, and these chips were converted to a powder of 150 µm or less in diameter by mechanical polishing. Analysis by the BET method revealed that the specific surface area of the Ni₃Al powder thus prepared was 2.3 m²/g.

Then, the powder thus prepared was treated with the following alkali and acid.

(1) 3 g of the Ni₃Al powder prepared by mechanical polishing was added into 120 g of an aqueous 20% NaOH solution, and the mixture was left at a temperature of 65 to 70°C for 5 hours while stirred. Then, the aqueous alkaline solution was removed by decantation. The precipitate was washed with distilled water in a suitable amount, and the wash liquid was removed by decantation. The operations were repeated until the wash liquid became neutral. The precipitate obtained was dehydrated. After dehydration, the precipitate was

dried at 50°C overnight, to give a Ni₃Al catalyst. ICP emission spectrochemical analysis revealed that about 14% (weight ratio) of Al in the Ni₃Al catalyst prepared with the aqueous NaOH solution was dissolved and removed. Measurement of the specific surface area by the BET method revealed that the specific surface area of the catalyst thus prepared was 5.1 m²/g.

(2) 1.3 g of the Ni₃Al powder prepared by mechanical polishing was added into 80 g of an aqueous 30% NaOH solution, and the mixture was left at a temperature of 60 to 65°C for 3.5 hours while stirred. ICP emission spectrochemical analysis revealed that about 10% (weight ratio) of Al in the Ni₃Al catalyst prepared with the aqueous NaOH solution was dissolved and removed. Measurement by the BET method revealed that the specific surface area of the powder thus prepared was 4.3 m²/g.

(3) 3 g of the Ni₃Al powder having a particle diameter of 32 to 75 μm or less prepared in the rotating disk atomization process was added to 120 g of a 20% HCl solution and left at room temperature for 3 hours while stirred. Measurement by the BET method revealed that the specific surface area of the powder prepared was 1.1 m²/g.

(4) 3 g of the Ni₃Al powder having a particle diameter of 32 to 75 μm prepared in the rotating disk atomization process was added to 120 g of a 5% HNO₃ solution, and the mixture was left at room temperature for 3 hours while stirred. Measurement by the BET method revealed that the specific surface area of the powder thus prepared was 3.6 m²/g.

The specific surface areas (m²/g) of the powders prepared by the surface treatment as measured by the BET method are summarized in Table 1 (the symbol "-" means no measurement).

【Table 1】

Sample	Before surface treatment	After 20 % NaOH treatment	After 30 % NaOH treatment	After 20 % HCl treatment	After 5 % HNO ₃ treatment
Ni ₃ Al (prepared by mechanical polishing)	2.3	5.1	4.3	-	-
Ni ₃ Al (prepared in rotating disk atomization process, 32 to 75 μm)	0.4	-	-	1.1	3.6

The results in Table 1 show that both alkali and acid treatments are effective in increasing the specific surface area of Ni₃Al.

<Example 2>

0.2 g of the powder sample prepared by mechanical polishing in Example 1(b) above was subjected as catalyst to a hydrogen reduction treatment at 240°C for 1 hour in a catalytic reactor [fixed bed-flow reactor], and the activity of the powder sample was evaluated under atmospheric pressure at reaction temperatures of 240°C, 260°C, 280°C, 300°C, 320°C, 340°C, and 360°C, by using a liquid mixture of methanol and water (CH₃OH:H₂O: 1:1.5 (mol)) as the raw material. The results are shown by black circular marks in FIGS. 1 to 3. As shown in FIG. 1, the hydrogen-production rate (ml/min/g) in the reaction increases as the temperature rises, but the rates are lower altogether. FIGS. 2 and 3 respectively show the CO- and CO₂-production rates (ml/min/g) at each reaction temperature measured as a function of the reaction temperature. Apparently, the Ni₃Al catalyst generated mainly CO, indicating that the Ni₃Al catalyst was active in the methanol-decomposing reaction (CH₃OH → CO + 2H₂), namely, in the hydrogen-generating reaction.

<Example 3>

0.2 g of the catalyst, i.e., the powder sample prepared by mechanical

polishing in Example 1(b) above and treated with an aqueous 20% NaOH solution, was subjected to a hydrogen reduction treatment at 240°C for 1 hour, and the activity of the powder sample was evaluated. The results are shown by black square marks in FIGS. 1 to 3. As apparent from FIG. 1, Ni₃Al had a high hydrogen-production rate of 351 ml/min/g at 352°C. In addition, the alkali-treated Ni₃Al catalyst had a superior high-temperature activity, showing a further increased hydrogen-production rate as the temperature rose. FIGS. 2 and 3 also show that mainly CO was formed. The results above indicate that the alkali treatment of Ni₃Al leads to increase in catalytic activity.

<Comparative Example>

A powder of a commercially available Raney nickel (50 wt % Ni-50 wt % Al) was prepared in a similar manner to the above Examples, and subjected to an activity evaluation test. The results are shown by black triangular marks in FIGS. 1 to 3. As apparent from FIG. 1, the hydrogen-production rate of the Raney nickel catalyst increases at a temperature of 300°C or less as the temperature rises, but not at a temperature of 300°C or more.

【Industrial Applicability】

The present invention provides a methanol-reforming catalyst containing an intermetallic compound Ni₃Al that is superior in activity and selectivity even at a temperature of 350°C or more in the reaction producing a hydrogen-containing gas from methanol or a mixed liquid of methanol and water as the raw material, which would be applicable to the fuel cell of automobiles, new smaller and high-efficiency high-temperature reactor, and the like and used effectively in industrial applications.

【Brief Description of Drawings】

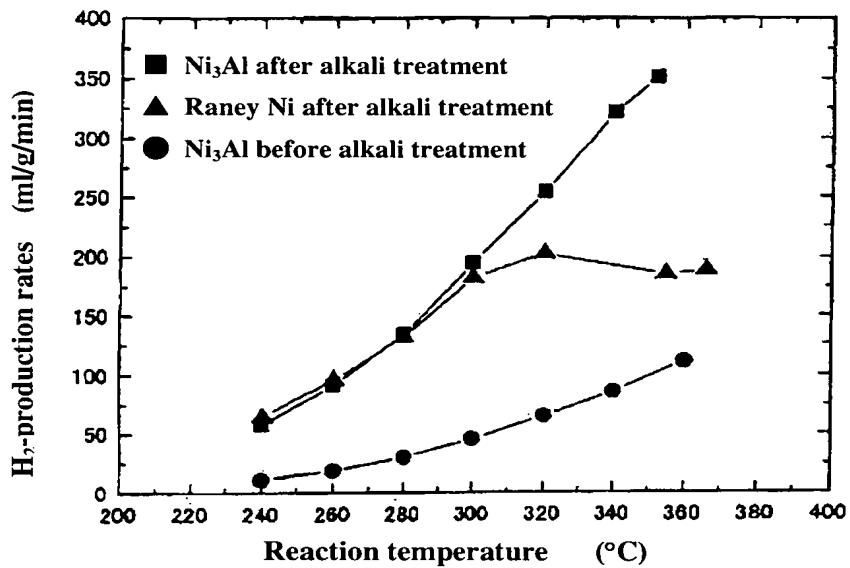
【Fig.1】 FIG. 1 is a graph showing the H₂-production rates (ml/min/g) measured in methanol-reforming reactions by using Ni₃Al and Raney nickel as a function of the reaction temperature.

【Fig.2】 FIG. 2 is a graph showing the CO-production rates (ml/min/g) measured in methanol-reforming reactions by using Ni₃Al and Raney nickel as a function of the reaction temperature.

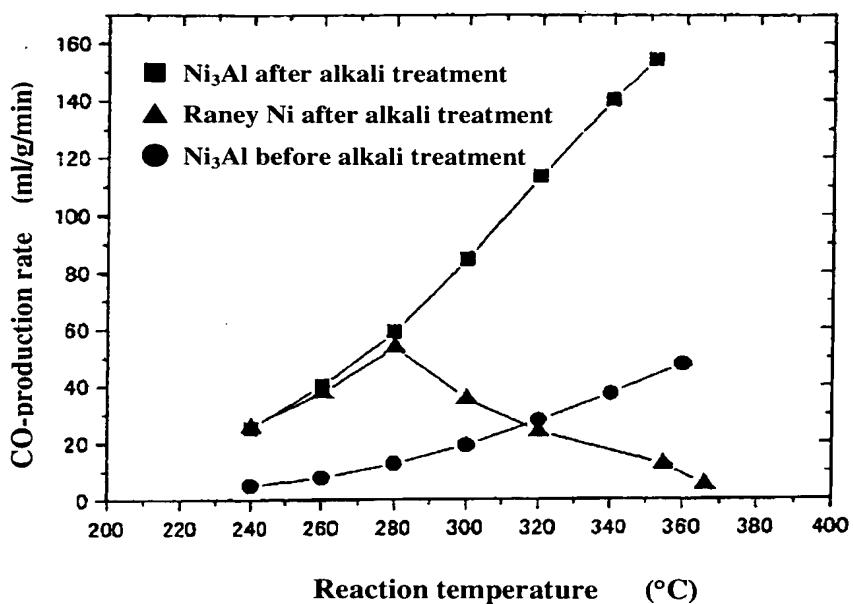
【Fig.3】 FIG. 3 is a graph showing the CO₂ production rates (ml/min/g) measured in methanol-reforming reactions by using Ni₃Al and Raney nickel as a function of the reaction temperature.

[Title of the document] Drawing

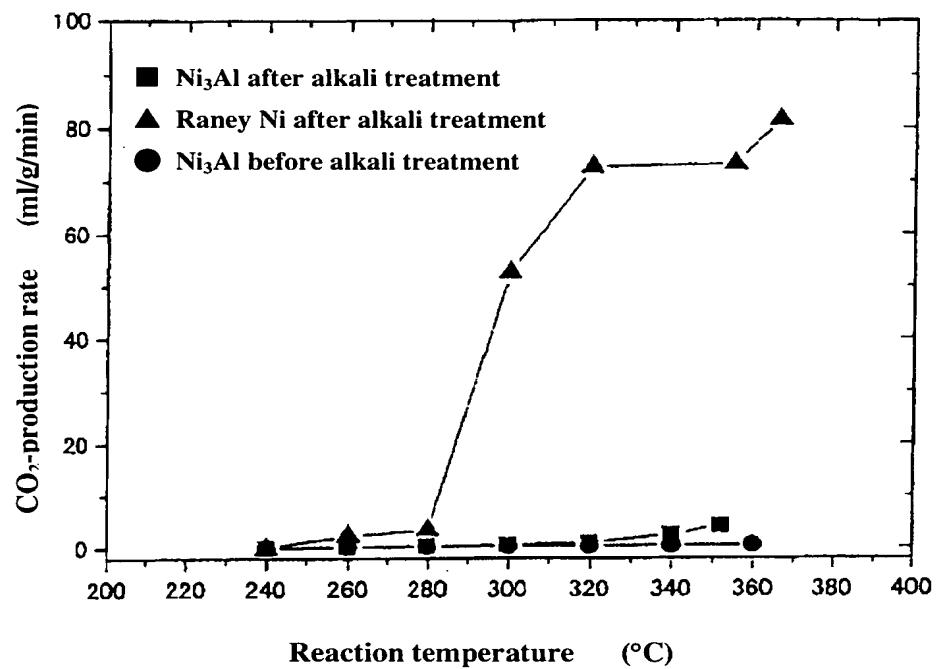
[Fig.1]



[Fig.2]



[Fig.3]



[Title of the document] Abstract

[Abstract]

[Problem] The invention of the present application aims to provide a methanol-reforming catalyst which is superior in heat resistance and abrasion resistance and has a high activity and selectivity even at a high temperature.

[Means for resolution] The present invention provides a methanol-reforming catalyst containing a Ni₃Al intermetallic compound as a main component.

[Selected Figure] Fig.1